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Ammonium Nitrate as an Oxidant for Composite
Propellants: Part 1: Preliminary Considerations

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MINISTRY OF SUPPLY

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

REPORT NO. 5/R/54.

Ammonium Nitrate as an Oxidant for Composite
Propellants: Part 1: Preliminary Considerations

by

P.R. Freeman

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1. SUMMARY

The physical properties of ammonium nitrate are discussed from the point of view of its use as an oxidant in composite propellants. Some discrepancies in the literature are pointed out and an attempt is made to explain them.

The maximum specific impulse obtainable with a simple ammonium nitrate/fuel mixture is about 223 sec. The advantage of using oxygenated fuels is calculated for cases where, because of rheological considerations, more than 5 or 6 per cent. of fuel must be used.

Slight caking of ammonium nitrate may occur at relative humidities less than the theoretical value for water absorption and it is suggested that this may be due either to occluded moisture or to welding between crystals in contact. Gross pick-up of moisture occurs at relative humidities above about 50 per cent. so that control of humidity during the manufacture and filling of composite propellants containing ammonium nitrate is essential.

The effect of potassium nitrate on the 32.1°C . transition, and the possibility of the rate of transition being affected by moisture content, is discussed.

It is suggested that uncertainty regarding the thermal stability and corrosive properties of ammonium nitrate may be due to work carried out with impure salt, particularly salt containing occluded nitric acid.

The hazards involved in using ammonium nitrate and precautions to be adopted are briefly discussed.

2. INTRODUCTION

In recent times, both here and in the United States, an ever-increasing amount of attention has been directed towards the possibility of using ammonium nitrate as the oxidant in various types of composite propellant. Plant already exists in U.K. (unlike ammonium perchlorate) for the manufacture of ammonium nitrate from synthetic ammonia, large quantities being made annually. Its price is 2d or 3d a lb. compared with about two shillings a lb. for imported ammonium perchlorate.

Ammonium nitrate has other advantages over alternative oxidants. It appears to be the only one which offers the possibility of a completely smokeless propellant and, although energetically inferior to perchlorates, its performance is better than sodium nitrate which is its only rival in cheapness and availability.

During the last couple of years especially, therefore, the Explosives Research and Development Establishment has attempted to utilise ammonium nitrate as an oxidant in plastic propellants and has sponsored an extra-mural research contract with Messrs. Monsanto Chemicals Ltd., for the development of a rubbery type of composite propellant containing the salt. In addition, the "pressed charge" propellant compositions of Messrs. I.C.I., Ltd., contain appreciable quantities of ammonium nitrate and preliminary work is in progress in E.R.D.E. on similar materials consisting almost entirely of ammonium nitrate. In the U.S. much work on ammonium nitrate composite propellants appears to be going forward. Both Aerojets and the Jet Propulsion Laboratory have used ammonium nitrate and mixtures of ammonium nitrate and ammonium perchlorate as the oxidant

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in cured resin compositions. Phillips Petroleum, Standard Oil, and Thiokol Corporation are all working on ammonium nitrate/synthetic rubber propellants and at Atlantic Research Corporation the possibility of using ammonium nitrate as the oxidant in propellants made by the "Plastisol" process is under investigation.

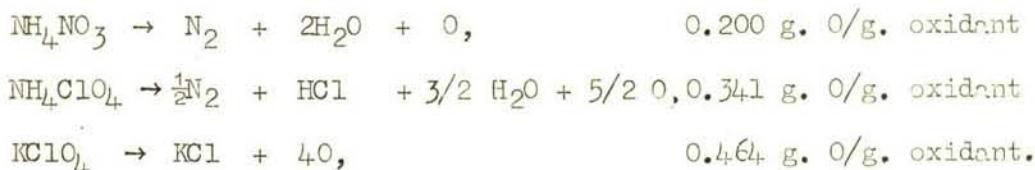
The object of this report is to discuss the physical properties of ammonium nitrate relevant to its use as an oxidant in composite propellants. It is intended in the near future to publish a report dealing with ammonium nitrate composite propellants under development at E.R.D.E., and also a bibliography on ammonium nitrate.

3. INTERNAL BALLISTICS

It has several times been stated that, owing to the economic advantages of using ammonium nitrate, some loss in performance, as compared with perchlorate propellants, could be tolerated. However, designers generally show little enthusiasm for a propellant having a specific impulse (S.I.) less than about 170 seconds, and almost invariably raise the requirement as time goes on. Thus as high an S.I. as possible should be aimed at, and it is worthwhile to consider the performance which might theoretically be obtained from ammonium nitrate compositions.

The maximum S.I. given by any mixture of fuel and oxidant depends upon the oxygen balance in regard to the formation of water and carbon dioxide and occurs slightly on the fuel-rich side of the stoichiometric mixture (1). This is shown in Fig. 1, in which theoretical values for the S.I. of various mixtures of ammonium nitrate and polyisobutene are plotted against the proportion of fuel used. This mixture has been chosen for its simplicity; it is not a practical propellant, lacking a combustion catalyst. On the fuel-rich side of stoichiometric the fall off of S.I. with increased fuel content is less marked, owing to the formation of methane and ammonia at low combustion temperatures. The corresponding curve for ammonium perchlorate/polyisobutene mixtures is included in Fig. 1 for comparison.

The 'decomposition equations' and the 'available oxygen per unit weight' for three common oxidants are as follows:-



The effect of the comparatively low oxygen content of ammonium nitrate on the proportions of fuel and oxidant required to give a balanced mixture is shown in Table 1 for three possible fuels, chosen to give a range of degrees of oxygenation in the fuel. The first is a linear hydrocarbon polymer $(-\text{CH}_2-)_n$, such as polyisobutene or polythene; the second a highly oxygenated polymer, $\text{CH}_{1.5}\text{O}_{0.5}$, such as polymethyl acrylate or polyvinyl acetate; the third is intermediate in degree of oxygenation, the polyester from propylene glycol and sebacic acid, $\text{CH}_{1.7}\text{O}_{0.3}$, being chosen as an example.

/Table 1

TABLE 1Stoichiometric Mixtures with Various Oxidants and Fuels

Oxidant	Fuel	Stoichiometric Mixture		
		% Oxidant	% Fuel	Ratio Oxidant:Fuel
NH_4NO_3	CH_2	94.5	5.5	17.2
	$\text{CH}_{1.7} \text{O}_{0.3}$	91.7	8.3	11.0
	$\text{CH}_{1.5} \text{O}_{0.5}$	89.4	10.7	8.3
NH_4ClO_4	CH_2	91.0	9.0	10.1
	$\text{CH}_{1.7} \text{O}_{0.3}$	86.6	13.4	6.5
	$\text{CH}_{1.5} \text{O}_{0.5}$	83.1	16.9	4.9
KClO_4	CH_2	88.2	11.8	7.5
	$\text{CH}_{1.7} \text{O}_{0.3}$	82.7	17.3	4.8
	$\text{CH}_{1.5} \text{O}_{0.5}$	78.4	21.6	3.6

The fact that larger quantities of ammonium nitrate are required to give balanced mixtures is a considerable disadvantage since rheological considerations are just as vital as ballistics. For plastic and elastic types of propellant, the desired degree of plasticity or elasticity can only be obtained up to a certain salt content.

In addition to oxygen balance, the S.I. of a propellant depends upon the heats of formation of its constituents and the heats of formation, molecular weights and specific heats of the combustion products. The overall effect of these factors on S.I. is shown in Table 2 in which the S.I.s of stoichiometric mixtures of ammonium nitrate and various fuels are compared with the S.I.s of stoichiometric mixtures of ammonium perchlorate and the same fuels. Ammonium nitrate gives rise to specific impulses about 10 per cent. lower than those obtainable with ammonium perchlorate and the combustion chamber temperatures, at a pressure of 1000 p.s.i., are about 1000°C. lower.

/Table 2

TABLE 2

Specific Impulses and Combustion Temperature for
Oxidant/Fuel Mixtures in Stoichiometric Proportions

Oxidant	Fuel	T _c , °C.	S.I. sec.
NH ₄ NO ₃	CH ₂	2060	224
	CH _{1.7} O _{0.3}	1970	218
	CH _{1.5} O _{0.5}	2070	220
NH ₄ ClO ₄	CH ₂	3030	245
	CH _{1.7} O _{0.3}	2940	241
	CH _{1.5} O _{0.5}	2930	238

Note: The combustion chamber temperatures and specific impulse were calculated by the method described by Pike (2), heats of combustion of the polymer fuels being obtained by the method of Kharasch (3) for the monomer and corrected for heats of polymerization. Comparison between calculated and experimental values for polystyrene and polyisoprene justified this procedure.

The effect of the degree of oxygenation of the fuel on the S.I. over a range of fuel contents is shown in Fig.2. Curves for the same three fuels as previously considered are given and also a curve for ammonium nitrate/polyvinyl alcohol mixtures. Ammonium perchlorate/polyisobutene is included for purposes of comparison. It can be seen that these curves have different slopes, indicating that the relative effect of the fuel varies with the fuel content.

There is, at present, no method of calculating rates of burning from the thermodynamic properties of a propellant, but low calorimetric levels and low combustion chamber temperatures usually imply low rates of burning. Ammonium nitrate is no exception to this, since almost all the measured burning rates of propellants containing the salt as sole oxidant fall within the range 0.05 to 0.3 inch/sec. at 1000 p.s.i. Unless the range can be extended, the low burning rates must severely restrict the application of ammonium nitrate propellants.

Ammonium nitrate/fuel mixtures cannot be ignited without the aid of a catalyst for promoting thermal decomposition. A large number of such materials are mentioned in the literature, e.g. chromium sesquioxide and nitrate, ammonium and potassium dichromate, magnesium oxide, calcium oxide, ferric oxide, nickel oxide, ammonium chloride, cobalt powder and Prussian Blue. There is disagreement over the effectiveness of some of these materials, probably because of different experimental methods of assessment and because in some cases the mixtures contained ingredients other than ammonium nitrate and fuel. There is no doubt, however, that ammonium and potassium dichromates are particularly effective. At E.R.D.E. it has been found that chromium sesquioxide and vanadium

/pentoxide

pentoxide are very active catalysts. Prussian Blue and asbestos powder have some catalytic action, but magnesium oxide, manganese dioxide, cobalt powder and certain other 'catalysts' mentioned in the literature were found to be without effect upon simple nitrate/fuel mixtures.

4. CAKING AND HYGROSCOPICITY

Ammonium nitrate is deliquescent in moist air. According to Lowry (4), the vapour pressure of a saturated aqueous solution is 9.3 mm.Hg. at 20°C. and 11.6 mm. at 25°C., corresponding to relative humidities of 66 per cent. and 61 per cent. respectively.

Despite the theoretical figures, C.G. Lawson has quoted (5) the National Fireworks Corp. of America as stating that ammonium nitrate will pick up traces of moisture at humidities greater than 26 per cent. and from this he infers that certain types of propellant containing ammonium nitrate may have to be processed at such low humidities.

Experiments have been carried out at E.R.D.E. to check this statement. Samples of ammonium nitrate and of mixed crystals of ammonium nitrate with 10 per cent. of potassium nitrate were dried at 60°C. for 24 hours and stored for several days at a series of controlled relative humidities, obtained with various saturated salt solutions. No stringent temperature control was used, but the laboratory temperature did not vary more than two or three degrees from 23°C. The samples, after drying, were free flowing, the ammonium nitrate being about 40 mesh and the mixed crystals about 100 mesh. They were weighed each day and observations made on the degree of caking. Each sample weighed 5 g. and weighings were carried out to 0.0001 g., so that an absorption of about 0.002 per cent. should have been detected. The following results were obtained:-

TABLE 3

Absorption of Moisture by Ammonium Nitrate and Mixed Crystals

Relative Humidity, %	Time of Storage, days	% Moisture Absorption	
		Mixed Crystals	Ammonium Nitrate
20	5	nil	nil
44	5	nil	nil
47	5	nil	nil
51	5	nil	nil
52	5	0.02	0.02
58	5	0.045	0.02
66	4	0.88	0.20
75	5	10.0	4.8

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It can be seen that there was a small absorption of moisture at humidities rather lower than the theoretical value. On the other hand, absorption could not be detected at relative humidities much greater than the 26 per cent. referred to above.

In no case did samples remain completely free-flowing throughout the experiment, although the degree of caking obtained at 20 per cent. relative humidity was very small indeed, only a few crystals becoming loosely aggregated.

From 44 to 51 per cent. R.H. caking was distinct, but gentle tapping with the finger on the side of the glass container was sufficient completely to break up the aggregates. Rather more vigorous tapping was required with the samples at 52 and 58 per cent. R.H., while those kept at 66 and 75 per cent. caked into hard solid masses after one or two days. At the end of 6 days, the mixed crystals kept at 75 per cent. R.H. had completely dissolved.

The caking of crystalline materials is thought to be due to surface recrystallisation, resulting in the formation of micro-crystalline 'bridges' between the particles which effectively cement them together (6). It is rather difficult to see why the slight caking at lower than the critical R.H. should occur, unless the crystals, despite the drying procedure, still contained occluded moisture which migrated to the surface. This is a possible explanation, although the amount of moisture must have been minute since no loss in weight was detected in our experiments.

Mr. J.R.C. Duke of E.R.D.E. suggested that some degree of welding might take place between dry crystals in contact; the plastic character of ammonium nitrate crystals would facilitate point contacts developing into contacts between surfaces. The migration of ions across the interface might also be promoted by lattice irregularities which probably exist in ammonium nitrate owing to loss of ammonia during the preparation of the crystals. Another factor which may be of importance is the probable presence of small quantities of acid ammonium nitrate ($\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$) which melts at a low temperature and might function as a cement. Photomicrographs of slightly caked ammonium nitrate were made (Fig.3) and in them flat surfaces in close contact can be seen, but it is impossible to say whether these have resulted from plastic deformation or salt recrystallisation.

Whetstone (7,8) has shown that caking of ammonium nitrate below the 32°C . transition point can be prevented by the use of small quantities of certain dyestuffs, in particular 0.1 per cent. of Acid Magenta. The additional use of a surface active agent, designated 'A.S.2', is said to extend the temperature range over which the treatment is effective (9). The function of the dyestuff is to modify the habit of the crystal 'bridges', making them more fragile, so that the hardness of the bulk product remains low. Ammonium nitrate treated with Acid Magenta may still cake slightly, but the aggregated material can be readily broken down into discrete particles. This is similar to the caking observed with untreated material at relatively low humidities, but even at these humidities it is found that with Acid-Magenta-treated material caking is less apparent than with untreated salt. This may indicate that the mechanism of caking at low humidities is the same as at high, but it is also possible that the dyestuff forms a barrier to migration of ions across the interface and so reduces welding.

Another method of preventing caking is to waterproof the crystals in some way; in the patent literature there are many examples of this. In general, these involve coating the particles with a water-repellant material, and a great variety of substances have been proposed for this, including paraffin wax,

2,2-dinitropropane

2,2-dinitropropane (10), zinc tetrammine nitrate (11), vegetable oil cake powder, calcium carbonate, diatomaceous earth and kaolin. The use of zinc tetrammine nitrate is of interest as affording an example of the disagreement often found in the literature on ammonium nitrate. According to the patent quoted, ammonium nitrate is treated with zinc oxide to give a product believed to be zinc tetrammine nitrate. This prevents caking when 0.25 to 5 per cent. is either added with agitation to granular ammonium nitrate or produced in situ on the nitrate. Whetstone (8), on the other hand, quotes zinc tetrammine nitrate as a chemical which increases the rate of water absorption by ammonium nitrate.

A specific coating method is the treatment of the crystals with 1 per cent. of methyltrichlorosilane, then heating to drive off hydrogen chloride, leaving a water-repellant coating of a silicone. This process has been tried by Messrs. Monsanto Chemicals, Ltd., who find that the treated salt does not cake hard when kept in partly filled bottles under normal storage conditions; when sprinkled on water it floats for an appreciable time before dissolving.

Yet another method of preventing, or helping to prevent, the caking of ammonium nitrate is to alter the shape of the particles, either by modification of the crystal habit or by the formation of small spherical particles or aggregates. The crystal habit can be modified by crystallising in the presence of various foreign materials, and Zabolotskii (12) lists a number of ions which, in concentrations of 0.05 to 0.1 mol./litre, cause the salt to crystallise in an equant rather than an acicular form. Acicular crystals are, however, only obtained by crystallisation at comparatively low temperatures and the normal commercial material is in the form of small equant crystals obtained by vacuum crystallisation at a comparatively high temperature (160° or 170°C.). The equant shape is retained at ambient temperatures despite passage through the transition point and caking is less with this material than with acicular crystals owing to the smaller extent of surface contact. Other commercial methods of preparation, which are especially in favour in countries where ammonium nitrate is used as a fertilizer, are the 'graining' and 'prilling' processes (13, 14, 15), which also give spherical particles or aggregates, although these are much larger than the usual crystallised material. In the former process the solution is concentrated to 98 per cent. and then cooled with continuous stirring, whilst in the latter process 98 per cent. solution is sprayed down a tower against a counter-current of air at a lower temperature.

The graining and prilling processes are usually carried out in order to produce rather large granules, about 1/32 inch to 3/32 inch in diameter, for agricultural purposes and high explosives manufacture. Very much smaller particles are often required for propellant manufacture, but it should not be impossible to modify the processes described so as to produce the required size (e.g. in the prilling process an atomising spray might be used). If the particle size of the product could be controlled closely enough, it should be possible to obtain the salt in the form of very small particles which would require no further milling or grinding before use in composite propellant. This would be a considerable advantage, since milling of ammonium nitrate to a smaller specific surface than about 2,000 cm.⁻¹ has proved rather difficult, perhaps owing to the plastic nature of the salt causing rapid crystal aggregation.

There appears to be disagreement over the extent to which ammonium nitrate can be dried. According to Early and Lowry (16), moisture is retained even when drastic drying methods are used and Mellor (17) refers to work in which drying over phosphorus pentoxide gave a moisture content of "less than 0.1 per cent." but was accompanied by decomposition, as evidenced by a smell of nitrogen oxides. Mellor also quotes an experiment in which ammonium nitrate was heated at 100°C. in one limb of an inverted U-tube, the other being cooled

/to

to -80°C . Water was continuously collected in the cooled limb but the moisture content of the salt remained unchanged, demonstrating a decomposition with production of water. On the other hand, experiments have been quoted (18) in which mixed crystals of ammonium and potassium nitrates (reputed by various authors to be more difficult to dry than pure ammonium nitrate) were dried to a 0.02 per cent. moisture content over P_2O_5 , and C.G. Lawson (5, 19) reports that Phillips Petroleum Company dry ammonium nitrate to a 0.03 per cent. moisture content and that other users in America work to 0.003 per cent. as determined by Fischer titration. At E.R.D.E. it has been observed that drying at 60°C . or 80°C . in an oven produces some slight decomposition or sublimation (a white deposit was noticed). A sample which was heated at 60°C . and weighed at intervals showed a loss of 0.001 per cent. per day after 5 weeks heating. There is evidence that the extent to which ammonium nitrate, or ammonium potassium nitrate, can be dried depends upon the degree of purity of the salt. (second report of this series - in preparation).

The question of the dryness of ammonium nitrate used in composite propellants is of considerable importance since the physical, and perhaps also the ballistic, properties of some types of composite propellant may depend markedly upon the moisture content. Thus, with plastic propellant containing ammonium nitrate the presence of more than about 0.2 per cent. of moisture has a very deleterious effect on the physical properties; in the complete absence of moisture the processed material is crumbly.

There are indications that the strength of certain types of "pressed charge" is increased by the presence of small amounts of moisture. As will be discussed later, there is evidence that the speeds of crystal traditions, particularly those in ammonium/potassium nitrate, are considerably affected by moisture, and this factor, too, may alter the physical and rheological properties of the propellant.

It is thus clear that in the manufacture of ammonium nitrate composite propellants the relative humidity will have to be controlled at less than 60 per cent. and that some form of water-proofing of the crystals or anti-caking treatment may be required. Whatever the degree of drying obtained or the humidity control found necessary, it will be essential for rocket motors containing these propellants to be carefully and thoroughly sealed against ingress of moisture.

5. THERMAL STABILITY, CORROSION, AND HAZARDS

Another point on which there is variance in the literature is the effect of small quantities of impurities on the thermal stability of ammonium nitrate. For instance, some authors claim that small quantities of urea stabilise the material (20) while others have been unable to confirm this (21). But there is no doubt that a number of substances, particularly chlorides and cellulosic material in general (e.g. wood meal) and starch, sensitise the decomposition. In their presence, carbon dioxide and nitrogen are evolved at comparatively low temperatures, whereas the pure dry salt can be heated at 100°C . for a long time without appreciable decomposition (22).

Aqueous solutions of ammonium nitrate readily evolve ammonia when heated and become progressively more acidic so that the solid material obtained by evaporation will contain an excess of nitric acid. It is probable that thermal stability, sensitivity to foreign materials and corrosive properties all depend to some extent upon the acidity of the particular sample of salt examined and this may account for some of the widely divergent observations.

According to Scott and Grant (23), fused ammonium nitrate will react with copper, aluminium, tin, lead, antimony, bismuth, nickel, silver and cadmium,

/but

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but Hodgkinson and Coote (24) state that aluminium is not attacked and Emmet (25) that tin is not attacked. Thorpe's "Dictionary of Applied Chemistry" states that ammonium nitrate will react with tin under certain conditions to form basic nitrates which are sensitive to heat and shock (cf: next paragraph).

There is disagreement about some of the corrosive properties of aqueous solutions and moist crystals. Thus some observers state that iron is not attacked whereas according to Ramann (26), ferric nitrate and nitrite are formed. Copper, cadmium, zinc, magnesium and lead are all said to be attacked by moist crystals. In the case of copper, and alloys containing copper, there is no doubt that there is attack even by fairly dry ammonium nitrate at normal temperatures, a bright greenish-blue deposit being formed on the surface of the metal. Bassett and Durrant (27) state that the presence of oxygen is necessary for this to happen and that the products are mainly blue cupric tetrammine nitrate, green basic nitrate, and some nitrite and tetrammine nitrite. The tetrammine nitrate and nitrite are said to be comparatively sensitive explosives. This corrosion of copper and copper alloys is of importance to the propellant manufacturer since it rules out the use of the bronzes which, owing to the spark hazard with steel, are his traditional materials for plant construction.

With regard to the hazard of handling ammonium nitrate and propellants in which it is a constituent, it would appear from the mass of information on the subject, that with the pure commercial salt there is no danger of explosion, either by heat or mechanical shock, in the absence of confinement. Detonation has not been obtained with the friction pendulum test up to 180°C. and heating the salt to 1000°/1500°C. by an electric arc between electrodes made of ammonium nitrate, merely caused fusion and violent boiling (28). Under confinement, the application of heat to the salt has been said to produce explosions at a temperature of 250°C., but the degree of confinement is probably of importance and there is no evidence whether or not localised heating in a confined mass would give rise to a propagating detonation (29). There is marked disagreement over the tendency for pure ammonium nitrate under confinement to propagate detonation when initiated by an explosive charge. Again, the degree of confinement and also the size of charge and particle size of the salts are of importance. Experiments carried out at E.R.D.E. show that no propagation occurs with light confinement, as obtaining with glass or thin-walled metal tubing, but propagation of detonation in commercially pure NH_4NO_3 was obtained in mild steel tubes, $1\frac{1}{2}$ inch diameter and $3/16$ inch wall thickness.

Mixed with fuels or with materials which catalyse its thermal decomposition, detonation of ammonium nitrate will take place much more readily. The disastrous explosions on record have almost all occurred with impure ammonium nitrate. The salt mixed with a few per cent. of petroleum jelly has been known to detonate on heating under a degree of confinement insufficient for detonation of the pure substance. Cook and Talbot (3) have pointed out that mixtures of ammonium nitrate with petrolatum or paraffin wax show maximum sensitivity at between 0.75 and 1.5 per cent. of the hydrocarbon. The latter is thought to sensitise the decomposition by acting as a fuel and to desensitise it by acting as a lubricant or buffer between the crystals. The 'fuel' effect alone would give a maximum sensitivity at oxygen balance (5.4 per cent.), but the 'lubrication' factor, increasing with hydrocarbon content, causes the maximum to occur at a much lower figure. The same authors stress the sensitising effect of bagging paper or cellulose. Ammonium nitrate/hydrocarbon mixtures normally explode in the region of 270° to 350°C., but in the presence of cellulose the explosion temperature may be lowered to 150°C.

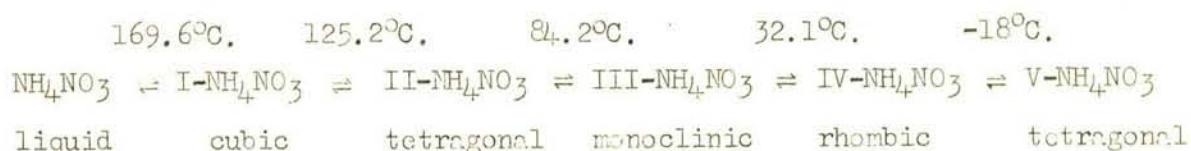
Despite the increased sensitivity obtained by mixing ammonium nitrate with a fuel, such mixtures are relatively insensitive compared with, say, ammonium perchlorate/fuel compositions, and will not explode when subjected to the usual impact, friction, flame, spark and shock tests at ordinary temperatures. It is, of course, necessary to ensure freedom from contamination by oil, grease, cellulosic material and other organic matter during salt processing (e.g.,

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grinding and drying), and it is also essential to test all proposed propellant ingredients for their effect on thermal decomposition before attempting to use them. Provided these precautions are taken, manufacturing processes in which there is no element of confinement (e.g., mixing and rolling) probably involve only a fire risk at worst. Under confinement, as in charge pressing, there is a small but definite explosion hazard, and the usual precautions, such as remote control operation from behind adequate screens, are called for.

6. CRYSTAL TRANSITIONS

Ammonium nitrate undergoes a number of crystal transitions which can be represented:



The most important of these from the point of view of propellant manufacture is the 32.1°C. transition, but the -18°C. transition will also be of importance in propellants expected to function over a wide temperature range. The 32.1°C. transition is accompanied by a large change in density, from 1.65 at 32°C. for III-NH₄NO₃ to 1.72 at 32°C. for IV-NH₄NO₃, corresponding to an expansion on heating of 0.0225 ml./g. With certain types of composite propellant the change would be expected to produce a very adverse effect on physical properties. On the other hand, a rubbery matrix might be able to accommodate volume changes in the filler without marked effect.

According to Allmand(31), the 32°C. transition can be depressed by using mixed crystals of ammonium nitrate with 9 per cent. of potassium nitrate. Allmand's method (32) was to evaporate a solution of the two salts to dryness at temperatures above 95°C., but, according to Messrs. I.C.I. Ltd. (33), the transition can be suppressed much more simply by merely heating an intimate mixture of the two salts together at any temperature between 32°C. and 100°C. for a time depending upon the temperature, the degree of subdivision, the intimacy of admixture and the moisture content. It has been shown at E.R.D.E. that the moisture content is all-important and that transformation into mixed crystals having the III-form can take place at temperatures below 32°C. Thus, an intimate mixture of the thoroughly dried salts was heated at 60°C; samples were withdrawn periodically, cooled to room temperature, and examined by X-ray powder photography. No change of crystal habit was detected after heating for 300 hours. The same crystal mixture was then allowed to take up 0.1 per cent. of moisture in a constant humidity enclosure at 25°C. Examination by X-ray powder photography showed that this was sufficient to give rise to almost complete transformation into the IV form.

Roffey et al. (34) state that a solid solution is preferable but not essential, the transition temperature being lowered merely by using an intimate mixture of the two salts. They also state that the mixtures are more difficult to dry than ammonium nitrate alone, but that this can be achieved by alternately heating to 100°C. and grinding cold. According to the I.C.I. patent (33) this should transform the mixture into a solid solution. The same workers also found that the transition was affected by moisture and recommended that the mixed salts be dried to less than 1 per cent. moisture content.

The effect of moisture on the transitions of mixed crystals has been noted by others and some interesting comments are made in O.S.R.D. Report 1577 (18).

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The work of Campbell is quoted who found that a sample of mixed crystals containing 1.7 per cent. of water underwent transition after 1 week at 0°C., but that a dry sample remained unchanged after 1 week at -10°C., and was cooled in steps to -52°C. before transformation eventually took place. Suspension of the 32°C. transition has also been observed in pure dry ammonium nitrate, depending on the rate of heating or cooling (13).

The dependence of the rate of transition of mixed crystals on moisture content is of considerable importance since, if the effect really is considerable, the cracking of a composite propellant containing ammonium and potassium nitrates would depend upon the amount of water - i.e. upon the efficiency with which the rocket motor is sealed. It is therefore conceivable that in such cases faulty sealing might have serious consequences, even resulting in an explosion of the rocket on ignition.

Jaenecke, Hamacher and Rahlfs (35) have given a complete phase diagram for the system $\text{KNO}_3/\text{NH}_4\text{NO}_3$. According to this, a 9 or 10 per cent. solid solution of potassium nitrate in ammonium nitrate becomes a two-phase system at about 18°C. consisting of solid solutions of potassium nitrate in both IV - NH_4NO_3 and III - NH_4NO_3 . The phase diagram shows that potassium nitrate depresses the initial transition temperature only slightly, to about 18°C., but that the transition is spread over a range of temperatures and is not complete above about -16°C. Furthermore, although no density figures are given, it is probable that the transition between the solutions involves a smaller density change than the transition between pure IV - NH_4NO_3 and III - NH_4NO_3 . Allmand (36) determined the effect of increasing quantities of potassium nitrate on the 32°C. transition of ammonium nitrate and evidently obtained inconsistent results since he quotes the inversion temperature with 10 per cent. potassium nitrate as being "7 ± 5°C. ??". The action of potassium nitrate in 'spreading out' the transition, as revealed in Jaenecke's paper, may explain this.

7. PLASTICITY OF CRYSTALS: DENSITY

Ammonium nitrate crystals (form IV) are much more flexible than those of most inorganic salts, and large crystals exhibit quite remarkable plasticity; a crystal of dimensions $1/2 \times 1/32 \times 1/32$ inch can be bent between the fingers into a circle without sign of fracture. This flexibility may prevent excessive breakdown of the crystals during rolling processes, as used in preparing plastic propellants and the type of elastic propellant under investigation by Messrs. Monsanto. From the point of view of ballistic control this is an advantage since the particle size of the oxidant usually has a considerable effect on the rate of burning and other ballistic characteristics of the propellant; excessive crystal breakdown during manufacture makes it difficult to obtain close control over the final particle size.

It has already been mentioned that, with certain types of composite propellant, the proportions of oxidant and fuel are governed primarily by rheological, not ballistic, considerations. In such cases, it is the volume of solids and not their weight which is of importance, so that with ammonium nitrate (density 1.725 g/ml.) a smaller weight of oxidant will be required to produce a given rheological condition than with ammonium perchlorate (1.954 g/ml.) or potassium perchlorate (2.521 g/ml.).

It is evident that as regards the proportions of oxidant and fuel in a propellant, rheological and ballistic requirements are in opposition. It is therefore considered unlikely that really high performance ammonium nitrate propellants will be obtained having elastic or plastic qualities. With the

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rigid type of composition these considerations do not apply and there appears to be no reason why S.I.s up to 220 sec. should not be realisable.

8. ACKNOWLEDGMENTS

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9. BIBLIOGRAPHY

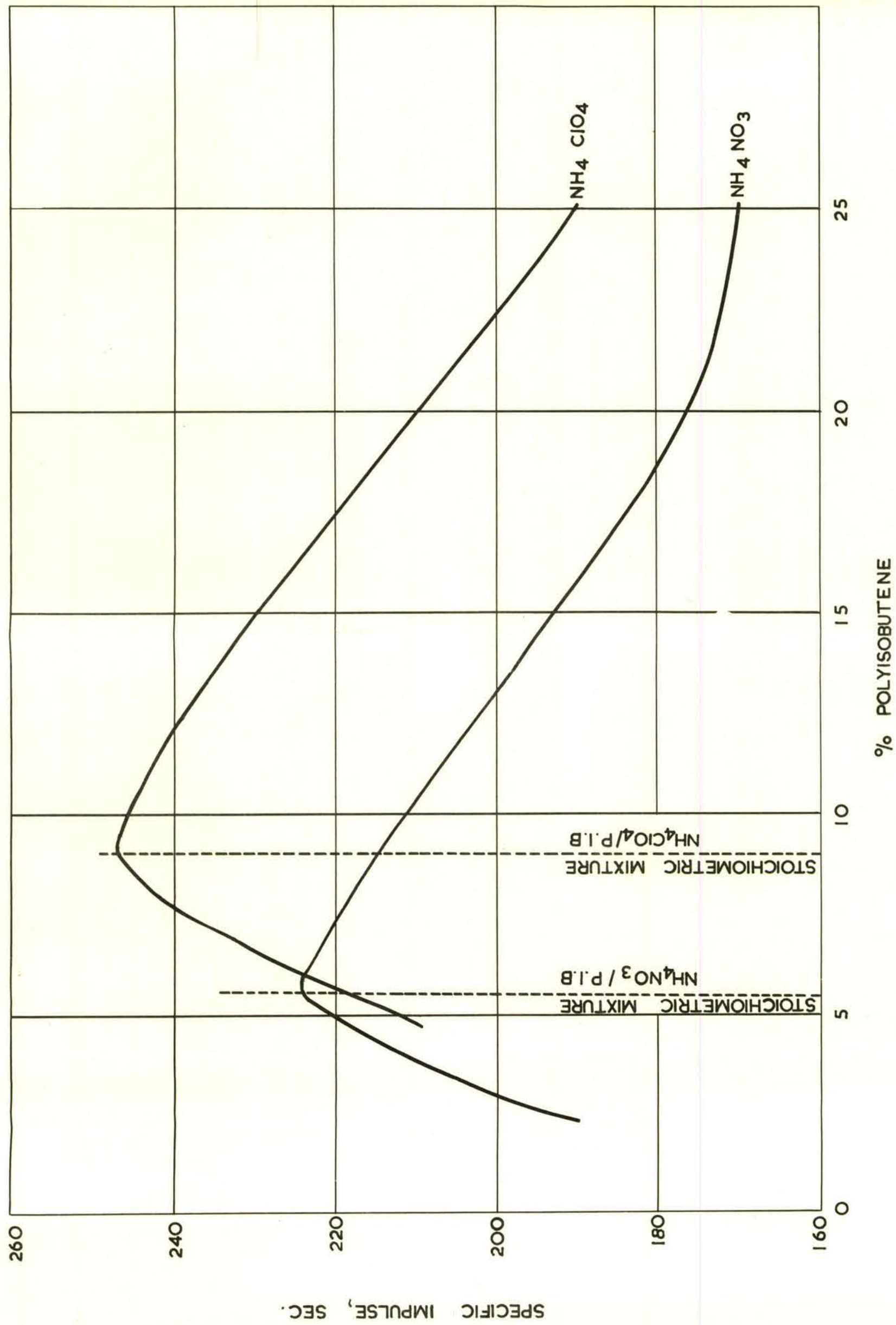
9. BIBLIOGRAPHY

1. C.G. Lawson, E.R.D.E. Technical Note No. 2/TN/53.
2. H.H.M. Pike, A.R.E. Report No. 25/49.
3. M.S. Kharasch, J.Res.Nat.Bur.Stand., 1929, 2, 359.
4. T.M. Lowry, "Report on Ammonium Nitrate. VI. Moisture in Ammonium Nitrate", W.D. Report, 1919.
5. C.G. Lawson, Private communication.
6. Lowry and Hemmings, J.Soc.Chem.Ind., 1920, 39T, 101.
7. J. Whetstone and I.C.I. Ltd., B.P.665,478; 627,680; 625,077.
8. J. Whetstone, Ind.Chem. Chem. Manuf., 1949, 401.
9. Idem., Ind.Eng.Chem., 1952, 44, 2663.
10. C.H. Goodale and Commercial Solvents Corp., U.S.P. 2,615,800.
11. J.H. Hauff, H.H. Holmes and Du Pont de Nemours and Co., B.P. 544,675.
12. T.V. Zabolotskii, J.Appl.Chem., U.S.S.R., 1950, 23, 1127.
13. W.H. Shearon and W.B. Dunworthy, Ind.Eng.Chem., 1953, 45, 496.
14. Du Pont de Nemours and Co., B.P.466,795.
15. Consolidated Mining and Smelting Co. of Canada, U.S.P. 2,402,192.
16. R.G. Early and T.M.Lowry, J.Chem.Soc., 1919, 115, 1387.
17. J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1946, Vol.2, Longmans Green and Co., London. p.829.
18. O.S.R.D. Report 1577.
19. C.G. Lawson, private communication.
20. F. Braconnier and A.H. Delsemme, Explosifs, 1952, 34.
21. M.L. Herquet, ibid., p.29.
22. Findlay and Rosebourne, J.Soc.Chem.Ind., 1922, 41T, 58.
23. G.S. Scott and R.L. Grant, U.S. Bureau of Mines Information Circular 7463.
24. W.R.E. Hodgkinson and A.H. Coote, Chem.News., 1904, 90, 142.
25. J.P. Emmet, Amer.J.Sci., 1930, 18, 255.
26. Ramann, Ber., 1881, 14, 1430.
27. H. Bassett and R.G. Durrant, J.Chem.Soc., 1922, 121, 2630.

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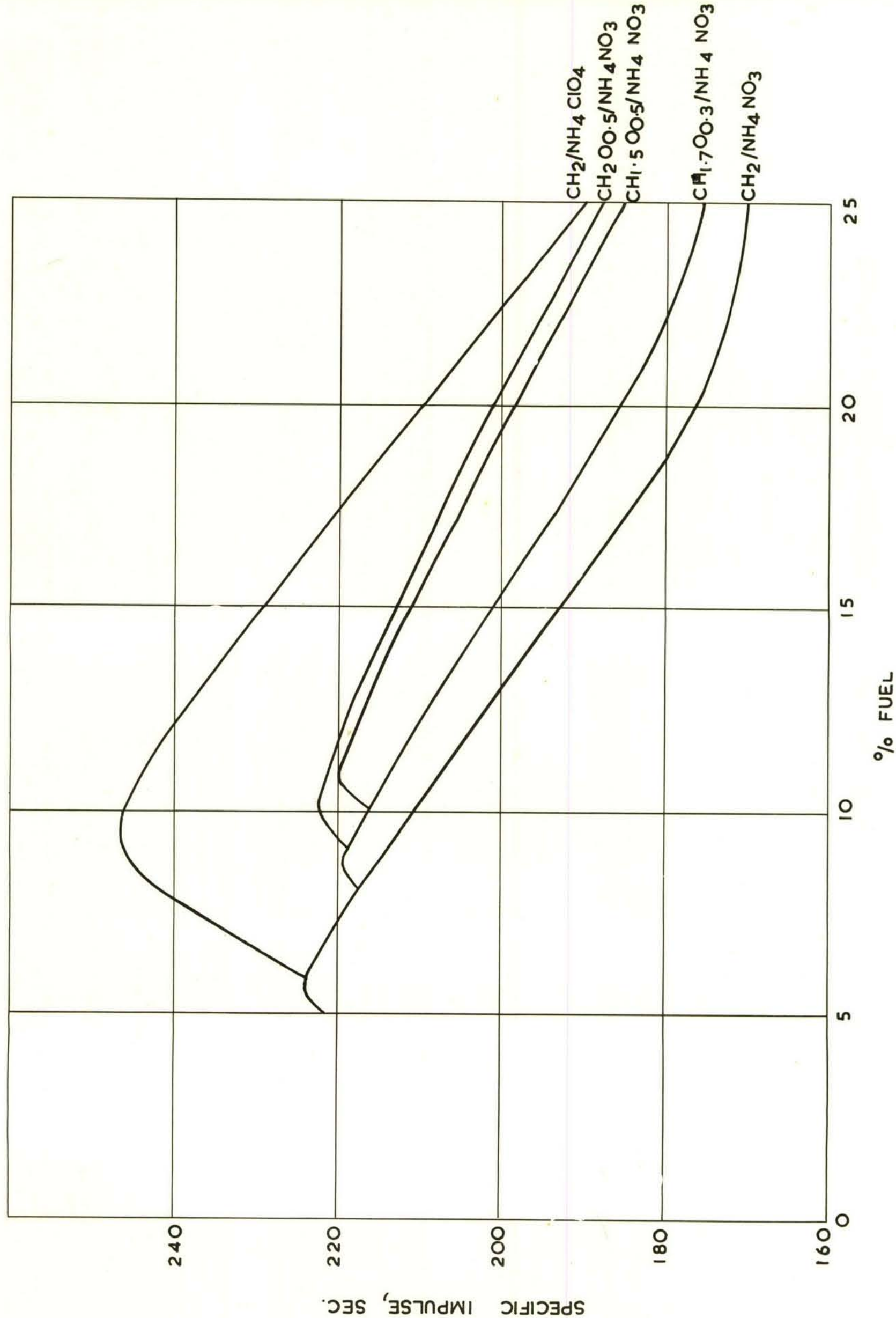
28. "Report of the Ammonium Nitrate Working Party", 1951, London, H.M.S.O.
29. L. Deffet, Explosifs, 1950, 90.
30. H.A. Cook and E.L. Talbot, Ind. Eng. Chem., 1951, 43, 1098.
31. A.J. Allmand, A.C.834, 1941, "Survey of Existing Literature on the Ammonium Nitrate Problem".
32. A.J. Allmand, A.C.973, 1941, "Supplementary Report on the Preparation of Potassium Nitrate-Ammonium Nitrate Mixed Crystals from Aqueous Solution".
33. J. Taylor and J. Whetstone, (I.C.I. Ltd.), B.P. 632,754.
34. F. Roffey, H.J. Poole, A.J. Allmand, et.al., B.P. 573,147.
35. Jaenecke, Hamacher and Rohlfs, Z.anorg. Chem., 1932, 206, 357.
36. A.J. Allmand, A.C.786, 1941, "The Elimination or Masking of the Volume Changes Associated with the NH_4NO_3 32°C. Transition Temperature".

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S.No. 368.BM.

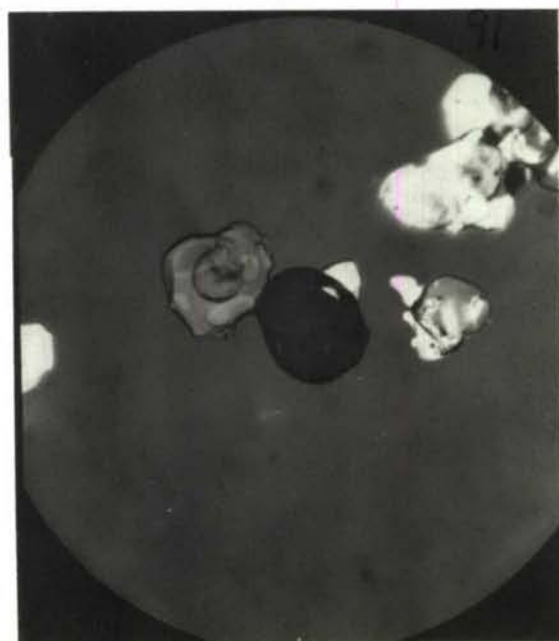


SPECIFIC IMPULSE OF NH_4NO_3 / P.I.B.
AND NH_4ClO_4 / P.I.B. MIXTURES. FIG. 1.

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PHOTOMICROGRAPHS (X 60) OF CAKED
AMMONIUM NITRATE PARTICLES. FIG. 3.

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The effect of potassium nitrate on the 32.1°C. transition, and the possibility of the rate of transition being affected by moisture content, is discussed.

It is suggested that uncertainty regarding the thermal stability and corrosive properties of ammonium nitrate may be due to work carried out with impure salt, particularly salt containing occluded nitric acid.

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P.R. Freeman

Sept., 1954

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The maximum specific impulse obtainable with a simple ammonium nitrate/fuel mixture is about 223 sec. The advantage of using oxygenated fuels is calculated for cases where, because of rheological considerations, more than 5 or 6 per cent. of fuel must be used.

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